

Determination of Benzene and Certain Derivatives in Water by Headspace Gas Chromatography (ISO 11423-1)

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Abstract

ISO 11423-1 describes specifications for the analysis of benzene and certain derivatives. This Application Note presents a method for their analysis using an Agilent Intuvo 9000 GC and 7697A Headspace sampler, which meets ISO-11423-1 criteria.

Introduction

The analysis of benzene and its derivatives in environmental water samples is usually proceeded by either headspace or purge and trap methods. The separation of these compounds is accomplished by gas chromatography (GC) with detection by a flame ionization detector (FID) or a mass spectrometric detector (MSD). ISO 11423-1 describes a headspace method for the determination of benzene and some of its derivatives in homogeneous samples of water and wastewater using GC.

Determination and confirmation of benzene and its derivatives can be achieved on a single system with the Intuvo 9000 GC and 7697A Headspace sampler. This Application Note demonstrates an injection onto dual capillary columns of different polarity and dual FIDs using inlet splitter technology. This system can easily achieve the performance specification for the compounds analyzed in method ISO 11423-1.

Experimental

Figure 1 demonstrates the inlet splitter technology. An Intuvo 9000 GC equipped with dual FIDs, and a 7697A Headspace sampler were used for this series of experiments. The sample was introduced to the SSL inlet by the headspace sampler, then divided into a 1:1 split onto two different columns by the splitter, and detected by their respective FIDs.

Table 1 describes the HS/GC/FID systems used for these experiments.

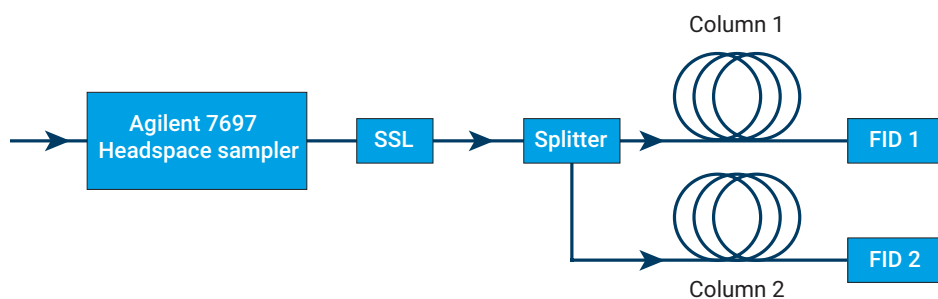


Figure 1. Intuvo system configured with splitter.

Table 1. Instrument conditions.

7697A Headspace sampler

Parameter	Value
Loop size	1 mL
Pressurization gas	Helium
Oven temperature	80 °C
Loop temperature	80 °C
Transfer line temperature	80 °C
Vial equilibration time	30 min
Injection Duration	0.5 min
Vial size	20 mL
Fill pressure	15 psi
Loop ramp rate	20 psi/min
Loop final pressure	10
Loop equilibration time	0.05

Intuvo 9000 GC

Parameter	Value
Inlet	250 °C, split 10:1
Guard Chip	200 °C
Bus temperature	200 °C
Column 1	Agilent J&W HP-5ms Ultra Inert, 30 m × 0.32 mm, 0.25 μm (p/n 19091S-413UI-HNT)
Column 2	Agilent J&W HP-INNOWax, 30 m × 0.32 mm, 0.25 μm (p/n 19091N-113I-HNT)
Carrier	Helium, 2 mL/min, constant flow
Oven	40 °C (8 minutes), then 7 °C/min to 150 °C (3 minutes), then 20 °C/min to 200 °C (5 minutes)
FID temperature	250 °C
Detector tail	250 °C
H ₂	30 mL/min
Air	400 mL/min
Make up (N ₂)	25 mL/min
Transfer line temperature	200 °C

Sample preparation

The stock solution was prepared by mixing 10 mL of methanol with 1 μL each of benzene and other required compounds in a 10-mL volumetric flask.

The intermediate stock solution was prepared by filling a 10-mL volumetric flask with 9 mL of methanol, and adding 1 mL of the stock solution.

Seven headspace vials were made at each calibration level by filling each vial with 10 mL of ultrapure water, and spiking varying amounts of stock solution and intermediate stock solution to achieve the required levels. The calibration standards were prepared at standard concentrations of 10 to 1,000 $\mu\text{g/L}$ (if 100 μL of stock solution is used, the concentration of benzene in this calibration solution is 878 $\mu\text{g/L}$). Table 2 shows the example of a series of calibration solutions. Table 3 shows the densities of benzene and a few derivatives. Table 4 shows the accurate mass concentration in the calibration solution for all compounds.

Table 2. Example of calibration solutions.

Measuring range ($\mu\text{g/L}$)	Amount of benzene in stock solution (μL)	Amount of benzene in intermediate stock solution (μL)	Mass concentration in the calibration solution for benzene ($\mu\text{g/L}$)
1,000	100	NA	878
600	60	NA	527
200	20	NA	176
100	10	NA	88
60	NA	60	53
20	NA	20	18
10	NA	10	9

Table 3. Densities of benzene and its derivatives.

Compound	Density (g/mL) at 20 °C
Benzene	0.878
Methylbenzene	0.867
1,2-dimethylbenzene	0.881
1,3-dimethylbenzene	0.865
1,4-dimethylbenzene	0.861
Ethylbenzene	0.867

Table 4. The accurate mass concentration in the calibration solution for all compounds.

Compound	L1 ($\mu\text{g/L}$)	L2 ($\mu\text{g/L}$)	L3 ($\mu\text{g/L}$)	L4 ($\mu\text{g/L}$)	L5 ($\mu\text{g/L}$)	L6 ($\mu\text{g/L}$)	L7 ($\mu\text{g/L}$)
Benzene	9	18	53	88	176	527	878
Toluene	9	17	52	87	173	520	867
Chlorobenzene	10	20	60	100	200	600	1,000
Ethylbenzene	9	17	52	87	173	520	867
<i>p</i> -Xylene	9	17	52	86	172	517	861
<i>m</i> -Xylene	9	17	52	87	173	519	865
<i>o</i> -Xylene	9	18	53	88	176	529	881
1,3,5-Trimethylbenzene	9	17	52	86	173	518	864
1,3-Dichlorobenzene	10	20	60	100	200	600	1,000
1,4-Dichlorobenzene	10	20	60	100	200	600	1,000
1,2-Dichlorobenzene	13	26	78	130	260	780	1,300
1,3,5-Trichlorobenzene	10	20	60	100	200	600	1,000
1,2,4-Trichlorobenzene	10	20	60	100	200	600	1,000
Naphthalene	10	20	60	100	200	600	1,000
1,2,3-Trichlorobenzene	10	20	60	100	200	600	1,000

Results and discussion

Primary and confirmation analysis from a single injection was accomplished using a dual FID GC system. To connect the two columns in the 9000 GC, an Agilent Intuvo inlet splitter chip was used, as opposed to a traditional Agilent Capillary Flow Technology 2-way splitter. Figure 2 shows the inlet splitter chip. Intuvo uses ferrule-free seals for all

fittings within the sample flowpath. The Intuvo Flow Chip is installed with a click of the torque drive without needing a ferrule. Furthermore, the Intuvo inlet splitter chip is fitted with a smart key, so that manual configuration is not necessary.

This Application Note evaluated a seven-level calibration curve set over the concentration range of 10 to 1,000 µg/L. An HP-5ms Ultra Inert column

(30 m × 0.32 mm, 0.25 µm) was used for primary analysis, and an HP-INNOWax column (30 m × 0.32 mm, 0.25 µm) was used for confirmatory analysis. The 1 mL sample from the 7697A Headspace sampler was split between two columns. Figure 3 shows an example chromatogram of the dual column analysis of target compounds with concentrations of approximately 200 µg/L.



Figure 2. Intuvo inlet splitter chip.

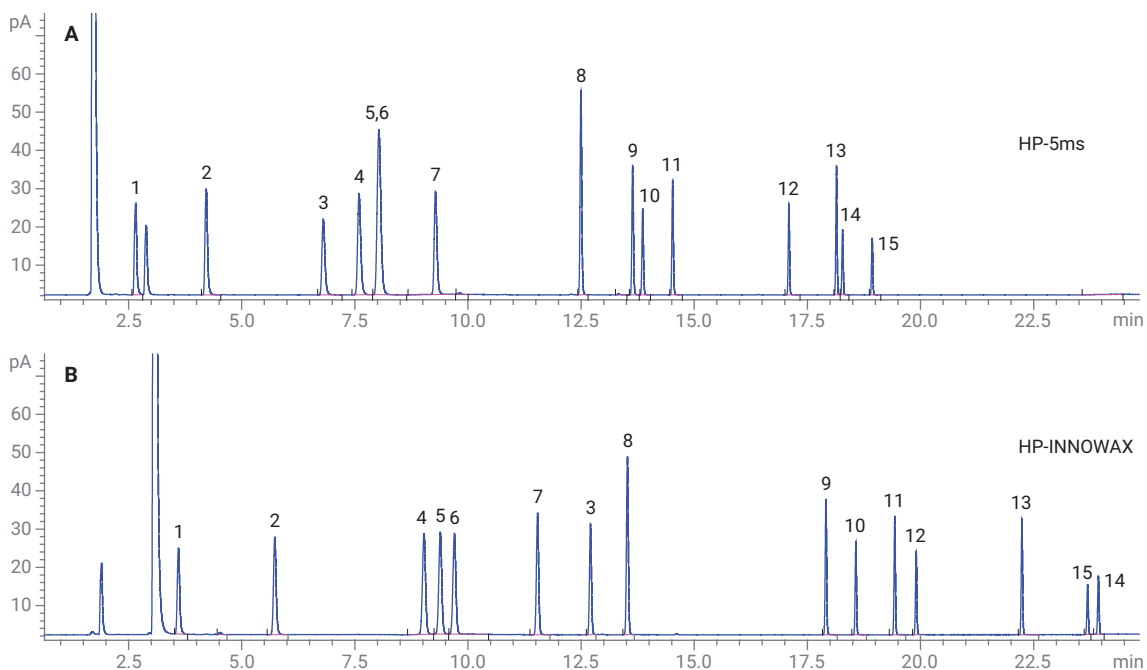


Figure 3. Chromatogram of the 15 target compounds (approximately 200 µg/L) on a dual column analysis using HP-5ms and HP-INNOWax capillary GC columns.

Table 5 lists the correlation coefficient for each of the compounds on both the HP-5ms and HP-INNOWax columns.

Linearity across the range studied gave R² values of 0.9991 or greater for all compounds on both capillary columns.

Repeatability (n = 7) was tested at approximately 10, 100, and 1,000 µg/L levels. The area %RSD was 1 to 4 %. For most compounds, the %RSD was well below 2.4 % at the 100 µg/L level on both columns.

Table 5. R² values for benzene and its derivatives in the calibration standard over the 10 to 1,000 µg/L range of this study (RT = retention time).

HP-5ms

Number	Compound	RT	CF formula	R ²
1	Benzene	2.66	Y = 0.497074x + 1.46853	0.9994
2	Toluene	4.22	Y = 0.609804x + 2.312781	0.9993
3	Chlorobenzene	6.81	Y = 0.445891x + 1.98473	0.9993
4	Ethylbenzene	7.61	Y = 0.712809x + 2.69980	0.9992
5, 6	<i>p</i> - and <i>m</i> -Xylene	8.06	Y = 0.691852x + 5.03299	0.9993
7	<i>o</i> -Xylene	9.3	Y = 0.627591x + 2.70487	0.9993
8	1,3,5-Trimethylbenzene	12.51	Y = 0.768776x + 2.99238	0.9992
9	1,3-Dichlorobenzene	13.64	Y = 0.39268x + 3.13867	0.9993
10	1,4-Dichlorobenzene	13.86	Y = 0.256386x + 1.37549	0.9992
11	1,2-Dichlorobenzene	14.52	Y = 0.253625x + 1.51839	0.9994
12	1,3,5-Trichlorobenzene	17.1	Y = 0.229307x + 1.16286	0.9992
13	1,2,4-Trichlorobenzene	18.15	Y = 0.318292x + 1.55345	0.9992
14	Naphthalene	18.28	Y = 0.16730x + 0.67331	0.9994
15	1,2,3-Trichlorobenzene	18.93	Y = 0.140687x + 0.63567	0.9993

HP-INNOWax

Number	Compound	RT	CF formula	R ²
1	Benzene	3.59	Y = 0.485755x + 1.30993	0.9994
2	Toluene	5.69	Y = 0.597445x + 2.32077	0.9993
3	Chlorobenzene	12.74	Y = 0.432706x + 2.27507	0.9993
4	Ethylbenzene	8.98	Y = 0.698082x + 2.47900	0.9993
5	<i>p</i> -Xylene	9.34	Y = 0.684834x + 2.43907	0.9993
6	<i>m</i> -Xylene	9.67	Y = 0.661928x + 2.40304	0.9993
7	<i>o</i> -Xylene	11.57	Y = 0.612867x + 2.96374	0.9992
8	1,3,5-Trimethylbenzene	13.56	Y = 0.750083x + 2.96220	0.9992
9	1,3-Dichlorobenzene	17.94	Y = 0.377563x + 1.92033	0.9992
10	1,4-Dichlorobenzene	18.59	Y = 0.251515x + 1.32254	0.9993
11	1,2-Dichlorobenzene	19.45	Y = 0.247633x + 1.37955	0.9994
12	1,3,5-Trichlorobenzene	19.93	Y = 0.223828x + 1.02772	0.9992
13	1,2,4-Trichlorobenzene	22.27	Y = 0.311953x + 1.58023	0.9991
14	Naphthalene	23.96	Y = 0.164970x + 0.691700	0.9994
15	1,2,3-Trichlorobenzene	23.72	Y = 0.136769x + 0.687123	0.9992

Signal-to-noise ratio (S/N) was used for method detection limit (MDL) calculation. A concentration of 2 µg/L standard solution was used to test the MDL, and the values for all compounds are listed in Table 6. For all compounds, the MDLs were ≤1.4 µg/L, which meet the specifications of the ISO 11423-1 method.

Method recoveries were measured by analyzing unspiked and spiked water samples. Standards containing benzene and its derivatives were spiked into tap water at a concentration of approximately 200 µg/L. Two parallel spiked samples were analyzed by the same method. Recovery was calculated using Equation 1.

Recovery ranges of two runs for each target compound at the 200 µg/L level are listed in Table 6, illustrating that the recovery results of 200 µg/L ranged from 95.3 to 102.5 %.

Table 6. RSD, MDL, and recovery percentages for benzene and its derivatives.

HP-5ms

No.	Name	RSD			MDL (µg/L)	Recovery %
		LOW (n = 7)	MID (n = 7)	HIGH (n = 7)		~200 µg/L (n = 2)
1	Benzene	2.4	1.9	1.5	0.5	96.3-98
2	Toluene	2.4	1.9	1.5	0.5	97.7-99.1
3	Chlorobenzene	2.3	2.1	1.8	0.8	95.8-97.7
4	Ethylbenzene	3.5	1.8	1.6	0.6	100-101.1
5, 6	<i>p</i> - and <i>m</i> -Xylene	3.7	1.9	1.6	0.4	98.8-100
7	<i>o</i> -xylene	3	2.1	1.8	0.6	98.2-99.9
8	1,3,5-Trimethylbenzene	3.6	1.9	1.8	0.3	101.7-102.5
9	1,3-Dichlorobenzene	3.7	2.1	1.7	0.4	96.4-97.3
10	1,4-Dichlorobenzene	2.3	2.4	1.9	0.8	95.7-96.7
11	1,2-Dichlorobenzene	2.2	2.1	1.7	0.6	97.4-99.2
12	1,3,5-Trichlorobenzene	3.5	1.9	2.3	0.7	100.6-101.1
13	1,2,4-Trichlorobenzene	3.1	1.9	2.1	0.5	100.1-100.2
14	Naphthalene	1.7	1.3	1.5	0.8	98.8-100.9
15	1,2,3-Trichlorobenzene	1.9	1.9	1.1	1.2	100.2-101.2

HP-INNOWax

No.	Name	RSD			MDL (µg/L)	Recovery %
		LOW (n = 7)	MID (n = 7)	HIGH (n = 7)		~200 µg/L (n = 2)
1	Benzene	1.9	1.8	1.5	1	96.1-97.3
2	Toluene	2.8	1.9	1.5	0.9	97.5-98.8
3	Chlorobenzene	2.5	2.1	1.8	0.9	96.3-97.9
4	Ethylbenzene	4	1.8	1.6	1	100.1-101.2
5	<i>p</i> -Xylene	3.3	1.9	1.6	1.1	99.3-100.2
6	<i>m</i> -Xylene	3.3	2	1.6	1	99.5-100.5
7	<i>o</i> -Xylene	2.9	2.2	1.8	0.8	97.9-99.5
8	1,3,5-Trimethylbenzene	3.7	1.9	1.8	0.6	101.6-102.4
9	1,3-Dichlorobenzene	2.6	2.2	1.9	0.8	96.7-97.7
10	1,4-Dichlorobenzene	2.3	2.4	1.9	1.2	95.3-96.5
11	1,2-Dichlorobenzene	2.3	2.1	1.8	0.9	97.8-99.6
12	1,3,5-Trichlorobenzene	2.5	1.8	2.2	1.3	100.6-101.2
13	1,2,4-Trichlorobenzene	3.2	2	2.1	0.9	100.1
14	Naphthalene	1.8	1.3	1	1.4	99-101
15	1,2,3-Trichlorobenzene	2.1	1.8	1.8	2	100.4-101.3

Equation 1.

$$\text{Recovery \%} = \frac{(\text{Conc. of spiked sample} - \text{conc. of unspiked sample})}{(\text{Conc. added})} \times 100$$

Conclusions

The test results of this study demonstrate that the Intuvo 9000 GC and 7697A Headspace sampler can easily achieve the performance specifications of ISO 11423-1. Correlation coefficients were found to be 0.9991 or better. The area RSD was 1 to 4 %. For most compounds, the MDLs were $\leq 1.4 \mu\text{g/L}$.

Reference

1. Water quality -- Determination of benzene and some derivatives – Part 1: Headspace gas chromatographic method. ISO 11423-1, **1997**.

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